

PATENT SPECIFICATION

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(54) ACID SALT SOLUTIONS

(71) We, BP CHEMICALS LIMITED, formerly BP Chemicals International Ltd., of Britannic House, Moor Lane, London EC2Y 9BU, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to novel compositions suitable for industrial, agricultural and pharmaceutical applications.

Hitherto saturated and unsaturated aliphatic carboxylic acids have only been sparingly used in industry and agriculture. The obnoxious odour of the free acids has made the handling of these acids unpleasant for the operatives and their corrosive nature has severely limited their use. It has been suggested in the past that this disadvantage may be overcome by employing the acids as their neutral salts or their esters. The obvious expedient of using the esters or neutral salts has been unsatisfactory since the acids on esterification or neutralisation lose a considerable amount of their activity.

It has now been found that by adding a base to an acid in aqueous solution in an amount which is less than the chemical equivalent required for full neutralisation, such compositions minimise to a substantial extent the odour and corrosivity of the acids without significant loss of activity of the free acid. In addition, it has surprisingly and unexpectedly been found that the bases and acids combine under these conditions to form complexes hereinafter referred to as 'complex acid salts' some of which are stable in aqueous solutions. Such complexes also have the added advantage that they exhibit negligible vapour loss relative to the free acids and hence retain the preservative activity on the substrate for a longer period of time.

Accordingly, the present invention is a liquid composition comprising in aqueous solution a complex acid salt as hereinbefore defined of ammonium ions and/or

ions of a metal selected from Group I and Group II of the Periodic Table due to Mendeleef, at least one carboxylic acid selected from formic acid, propionic acid, *n*-butyric acid, *iso*-butyric acid, 2-methyl butyric acid, valeric acid, levulinic acid, acrylic acid and methacrylic acid, the ratio of acid to ammonium and/or the metal ions being in the range of 2:1 and 4:1 on a chemical equivalent basis and the concentration of water in the aqueous solution being between 15 and 75% by weight of the total composition.

The Group I and Group II metals of the Periodic Table due to Mendeleef are preferably selected from sodium, potassium, calcium and magnesium. Although metal ions such as copper, strontium and beryllium may also be used, it will be clear that such compositions can only be used for certain special applications e.g. involving pesticidal or fungicidal activity, due to the known toxic nature of the cation. The chemical equivalent ratio of acid to cation is 2:1 and 4:1. The amount of each component would naturally vary within these ranges depending upon the nature of the cation and the intended use of the composition.

The minimum amount of water in the compositions of the present invention will depend upon the solubility of the complex acid salts contained therein. Thus the calcium and magnesium acid salts would be somewhat less soluble than the sodium and ammonium salts. The concentration of water is between 15 and 75% by weight of the total composition and suitably forms a homogeneous solution. The weights of the products are calculated as the mass weight of the product applied.

The compositions of the present invention may contain one or more complex acid salts. For example when ammonia is added to aqueous propionic acid the resulting composition may contain ammonium dipropionate as the complex acid salt. Similarly by suitable choice of cations and acid any number of complexes such as am-

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monium diformate, ammonium dibutyrate, ammonium diisobutyrate, sodium dipropionate, potassium dipropionate, calcium tetrapropionate and magnesium tetrapropionate may be present. Although the existence of some similar compounds has been reported in literature, there was hitherto no evidence that these were stable in aqueous solution nor indeed that such compounds exhibit enhanced beneficial activity when compared with the free acids. Their existence in solution has now been confirmed by Raman spectroscopy.

The complex acid salt may be prepared by mixing a carboxylic acid with a calculated amount of a base of the desired cation in an aqueous medium. For example, in preparing compositions containing the ammonium ion the acid may be mixed with a concentrated aqueous ammonia solution. On the other hand, for preparing compositions containing the calcium ion, a full calcium salt of the acid may be dissolved in an appropriate amount of the free acid or the free acid may be partially neutralised by lime or reacted with limestone.

The composition may be prepared prior to use or the acid and base components forming the composition may be added separately but simultaneously at the point of application.

The compositions of the present invention with a suitable cation may be used as a preservative for animal feedstuffs and agricultural crops to prevent growth of mould, bacteria and fungi. This may be achieved by applying the composition to the desired substrate as hereinafter defined.

Thus, according to a further embodiment, the present invention is a process for preserving substrates as hereinafter defined against microbial degradation comprising applying to the said substrate a liquid composition which is an aqueous solution of complex acid salts as described above.

By the term "substrate" is meant here and throughout the specification grass, agricultural crops and/or compounded animal feedstuffs and materials used in preparation thereof such as barley, wheat, oats, rye, maize, rice, hay, straw, silage, dried grass, tick beans, soya beans, bagasse, sunflower seed, sugar cane, rape seed, groundnuts, fish meal, meat and bone meal, buckwheat chaff and wood shavings. Animal excreta may also be treated by the present compositions.

The preservative compositions of the present invention may contain one or more complex acid salts or a mixture of the free acid and the acid salt which may be formed "in situ" during the preparation of the composition. The composition may also contain other conventional additives, in particular those with fungicidal or bacteriocidal

properties, such as formalin, formic acid, acetic acid, sorbic acid, dehydroacetic acid and bisulphites.

The amount of composition used for the preservation of a substrate would depend not only on the substrate to be preserved but also on the acidic and cationic ingredients thereof. For example, copper which is nutritionally valuable and is a known growth promoter in animal feed would be used in low concentrations. On the other hand, compositions containing ammonium ions can be used within a wide range of concentrations without any deleterious effect. Thus, the liquid compositions of the present invention when applied as a preservative to a substrate suitably contain between 0.1 and 5% of the inorganic complex acid salts based on the weight of the substrate treated. It is preferably between 0.1 and 2.5% by weight of the substrate treated. The liquid compositions may be applied to the substrates before, during or after harvest or to standing crops.

Other applications of the compositions of the present invention include use in industry for removal of scales from pipes and boilers. In the pharmaceutical industry one of the uses may be in the treatment of fungal infections such as athlete's foot. Such solutions also exhibit buffering activity and may find use in photographic applications. The ammonium and sodium ion containing solutions may be useful as antifreezes. Copper containing solutions may be used for example as wood preservatives and in vine fungicides.

The invention is further illustrated with reference to the following Examples.

EXAMPLES

Examples 1—14

In each example 100 g of barley, which has been remoistened to 30% moisture content (wet mass basis), was treated with the product under test, mixed thoroughly, then stored in a loosely capped bottle in a humidity cabinet maintained at 23°C and 100% relative humidity. Each treatment was carried out in duplicate or triplicate. The stored grain was examined regularly for the first appearance of mould growth.

The Examples were terminated after one year, at which time many of the samples were still mould-free (the time for mould to appear is shown as >365 days for mould-free samples).

The comparative tests A—G and the control experiments (X) were carried out under the same conditions as above except for using the appropriate free acid or fully neutral salts as indicated in the Tables below.

Examples 15—18

5 In these examples the compositions as shown in the table were applied during baling of moist hay (31% moisture content), the bales were then stacked and the stacks analysed for mould tests as shown.

10 The comparative test H and the control experiments (X¹) were carried out under the same conditions but without an additive and the free acids respectively.

Examples 19, 20 and Comparative Tests I—K

In each experiment 1 Kg. samples of

freshly cut lucerne silage (83% moisture content) were treated with the composition under test, and stored under anaerobic conditions in gas jars, for six months at 23°C. After six months ensilage the gas jars were opened and samples of the silage analysed for water soluble carbohydrates, free ammonia, *n*-butyric acid, and lactic acid. The odours of the silages were also noted. A criteria of good silage is an acceptable odour, high concentrations of water soluble carbohydrates and lactic acid, and low concentrations of free ammonia and *n*-butyric acid.

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EXAMPLES 1-14.

Barley (30% m.c.) Storage Data with Compositions

| Ex. No. | Composition Applied (Chemical Eqty. Ratio) Acid | Cation | Method of Application | Complex Identified | Treatment level % m/m of composition applied | Days to Mould | | |
|---------|---|-----------------------------------|--------------------------|-----------------------------|---|---------------|------|------|
| 1. | Propionic Acid 2 | NH ₄ ⁺ 1 | 80% Aq. Soln. | Ammonium dipropionate | 0.5 | 36 | 36 | 47 |
| 2. | Propionic Acid 2 | NH ₄ ⁺ 1 | " | " | 0.75 | >365 | >365 | >365 |
| 3. | n-Butyric Acid 2 | NH ₄ ⁺ 1 | " | Ammonium di-n-butyrate | 0.5 | 29 | 29 | 35 |
| 4. | n-Butyric Acid 2 | NH ₄ ⁺ 1 | " | " | 0.75 | 99 | 109 | 305 |
| 5. | n-Butyric Acid 2 | NH ₄ ⁺ 1 | " | " | 1.0 | >365 | >365 | >365 |
| 6. | iso-Butyric Acid 2 | NH ₄ ⁺ 1 | " | Ammonium di-iso-butyrate | 0.5 | 29 | 29 | 52 |
| 7. | iso-Butyric Acid 2 | NH ₄ ⁺ 1 | " | " | 0.75 | 93 | 93 | 109 |
| 8. | iso-Butyric Acid 2 | NH ₄ ⁺ 1 | " | " | 1.0 | >365 | >365 | >365 |
| (X) | Propionic Acid | - | " | - | 0.44 | 51 | >365 | - |
| (X) | " | - | " | - | 0.5 | >365 | >365 | - |

(X) - Control Experiment

EXAMPLES 1-14 (cont.)

| Ex. No. | Composition Applied (Chemical Eqvt. Ratio) Acid | Cation | Method of Application | Complex Identified | Treatment level % m/m of composition applied | Days to Mould |
|---------|---|-----------------------|--------------------------|---|---|---------------|
| 9. | Propionic Acid 2 | NH_4^+ 1 | 70% Aq. Soln. | Ammonium dipropionate | 0.21 | 15 |
| 10. | Propionic Acid 2 | NH_4^+ 1 | 75% Aq. Soln. | " | 0.23 | 16 |
| 11. | Propionic Acid 3 | NH_4^+ 1 | 70% Aq. Soln. | Ammonium dipropionate Propionic Acid. | 0.21 | 18 |
| G. | Propionic Acid 1 | NH_4^+ 1 | 70% Aq. Soln. | Ammonium propionate | 0.21 | 4 |
| 12. | Propionic Acid 2 | Na^+ 1 | 70% Aq. Soln. | Sodium dipropionate | 0.21 | 11 |
| 13. | Propionic Acid 2 | Ca^{++} 1 | 45% Aq. Soln. | Calcium tetra- propionate | 0.21 | 12 |
| 14. | Propionic Acid 2 | Mg^{++} 1 | 25% Aq. Soln. | Magnesium tetra- propionate | 0.21 | 13 |
| (X) | Propionic Acid | - | 70% Aq. Soln. | " | 0.21 | 27 |

G - Comparative Test

(X) - Control Experiment

COMPARATIVE TESTS

| Ex. No. | Composition Applied | Method of Application | Treatment Level % m/m of Composition Applied | Days to Mould | | |
|---------|----------------------|---------------------------|---|---------------|------|-----|
| A | Ammonium Propionate | As a 50% Aqueous Solution | 0.75 | 34 | 34 | 34 |
| B | Ammonium Propionate | As a 50% Aqueous Solution | 1.0 | 42 | 45 | 45 |
| C | Ammonium Butyrate | As a 50% Aqueous Solution | 0.75 | 34 | 34 | 42 |
| D | Ammonium Butyrate | As a 50% Aqueous Solution | 1.0 | 45 | 51 | 51 |
| E | Ammonium Isobutyrate | As a 50% Aqueous Solution | 0.75 | 35 | 37 | 37 |
| F | Ammonium Isobutyrate | As a 50% Aqueous Solution | 1.0 | 100 | 100 | 190 |
| (X) | Propionic Acid | As a 50% Aqueous Solution | 0.35 | 190 | >365 | — |
| (X) | Propionic Acid | As a 50% Aqueous Solution | 0.4 | 92 | >365 | — |
| (X) | Propionic Acid | As a 50% Aqueous Solution | 0.45 | >365 | >365 | — |

A to F — Comparative Tests

(X) — Control Experiment

EXAMPLES 15-18.

Summary of Compositions used for field trial with Hay

| Ex. No. | Composition Applied (chemical Eqvt. Ratio) Acid | Method of Application | Complex identified | Treatment level % m/m of Composition Applied | % loss of composition After 31 days | Mould Count (No./g) After 8 days | Mould Count (No./g) After 31 days |
|-------------------|---|-----------------------|---|--|-------------------------------------|----------------------------------|-----------------------------------|
| H | — | — | — | — | — | 21×10^3 | 53×10^3 |
| (X ¹) | Propionic Acid | 70% Aq. Soln. | — | 0.95 | 58.0 | 4.5×10^3 | 65×10^3 |
| (X ²) | " | 70% Aq. Soln. | — | 1.35 | 36.0 | <100 | <100 |
| 15. | Propionic Acid 2 | " | Ammonium Dipropionate | 0.98 | 0 | <100 | <100 |
| 16. | Propionic Acid 2 | " | " | 1.76 | 4.0 | <100 | <100 |
| 17. | Propionic Acid 3 | " | Ammonium Dipropionate, propionic acid | 0.98 | 30.0 | <100 | 5×10^3 |
| 18. | Propionic Acid 3 | " | " | 1.35 | 21.0 | <100 | <100 |

H — Comparative Test

(X¹) — Control Experiment

EXAMPLES 19 and 20.

| Ex. | Composition Applied Acid/Cation Chemical Equivalent Ratio | Complex Salt Identified | Method of Application | Treatment Level % v/m of Solution Applied | Chemical Analysis of Silage (% w/m) | | | | pH of Silage Juice | Odour of Silage |
|-----|---|-------------------------|------------------------|---|-------------------------------------|--------------|----------------|-------------|--------------------|-----------------|
| | | | | | Water Soluble Carbo-hydrates | Free Ammonia | n-Butyric Acid | Lactic Acid | | |
| 19 | 2 Formic Acid/ 1 NH_4^+ | Ammonium Diformate | As a 75% Aqueous Soln. | 0.34 | 0.10 | 0.22 | 0.01 | 0.39 | 5.17 | Acceptable |
| 20 | 2 Formic Acid/ 1 NH_4^+ | Ammonium Diformate | As a 75% Aqueous Soln. | 0.45 | 0.10 | 0.20 | 0.03 | 0.71 | 5.15 | Acceptable |
| I | 1 Formic Acid/ 0 NH_4^+ | — | As a 85% Aqueous Soln. | 0.34 | 0.10 | 0.15 | 0.04 | 0.62 | 5.08 | Acceptable |
| J | 1 Formic Acid/ 0 NH_4^+ | — | As a 85% Aqueous Soln. | 0.45 | 0.14 | 0.12 | 0.03 | 0.95 | 4.58 | Acceptable |
| K | None | — | — | — | 0.05 | 0.30 | 0.29 | Nil | 5.77 | Unpleasant |

I, J and K — Comparative Tests

The principal advantages of using the compositions of the present invention are that

- a) they are less caustic to skin and hence considerably safer to the operative,
- b) they are less corrosive to metals than the free acids,
- c) they do not remove paint and grease and so do not promote deterioration of equipment,
- d) they have a lower vapour pressure than the free acids and hence not only reduce environmental hazards due to evaporation but also make more efficient use of the preservative composition applied on the substrate,
- e) they do not attack soft seals and pipes and hence facilitate equipment design,

f) they reduce, and in some cases eliminate, the obnoxious odour of the preservative acids,

g) they are appreciably more active than the neutral salts and only marginally less active than the free acids,

h) they have a greater solubility in water than the neutral salts and hence facilitate formulation,

i) they can be used as a medium for introducing nutritionally beneficial cations into the substrates preserved.

The use or practice of the present invention as claimed and described herein in contravention of "The Preservatives in Food Regulations, 1975 (S.I. No. 1487)" is hereby disclaimed.

WHAT WE CLAIM IS:—

1. A liquid composition comprising in aqueous solution a complex acid salt as hereinbefore defined of ammonium ions and/or ions of a metal selected from Group I and Group II of the Periodic Table due to Mendeleef, at least one carboxylic acid selected from formic acid, propionic acid, *n*-butyric acid, *iso*-butyric acid, 2-methylbutyric acid, valeric acid, levulinic acid, acrylic acid and methacrylic acid, the ratio of acid to ammonium and/or the metal ions being in the range of 2:1 and 4:1 on a chemical equivalent basis and the concentration of water in the aqueous solution being between 15 and 75% by weight of the total composition.
2. A liquid composition according to claim 1 wherein the metal ions are selected from sodium, potassium, calcium and magnesium.
3. A liquid composition according to claim 1 wherein the metal ions are selected from copper, beryllium and strontium.
4. A liquid composition according to any one of the preceding claims wherein said liquid composition contains in solution at least one complex acid salt as hereinbefore defined selected from ammonium diformate, ammonium dipropionate, sodium dipropionate, potassium dipro-

pionate, calcium tetrapropionate, magnesium tetrapropionate, ammonium dibutyrate and ammonium diisobutyrate.

5. A liquid composition according to any one of the preceding claims wherein the composition contains in addition at least one additive selected from formalin, formic acid, acetic acid, sorbic acid, dehydroacetic acid and a bisulphite.

6. A liquid composition according to claim 1 as hereinbefore described with reference to the Examples.

7. A process for preserving substrates as hereinbefore defined against microbial degradation comprising applying to the said substrate a preservative liquid composition as claimed in any one of the preceding claims.

8. A process according to claim 7 wherein 0.1 to 5% of the liquid composition based on the weight of the substrate is used to treat the substrate.

9. A process for preserving substrates according to claim 7 as hereinbefore described with reference to the Examples.

10. Substrates as hereinbefore defined whenever preserved by a process according to any one of the preceding claims 7 to 9.

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